



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁷ : C09K 5/04	A1	(11) International Publication Number: WO 00/56834 (43) International Publication Date: 28 September 2000 (28.09.00)
(21) International Application Number: PCT/US00/07546 (22) International Filing Date: 22 March 2000 (22.03.00) (30) Priority Data: 60/125,510 22 March 1999 (22.03.99) US Not furnished 21 March 2000 (21.03.00) US (71) Applicant: E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US). (72) Inventors: BIVENS, Donald, Bernard; 210 West Locus Lane, Kennett Square, PA 19348 (US). MINOR, Barbara, Hav- iland; 233 Greenhaven Drive, Elkton, MD 21921 (US). YOKOZEKI, Akimichi; 109 Congressional Drive, Apart- ment C, Wilmington, DE 19807 (US). (74) Agent: EDWARDS, Mark, A.; E.I. Du Pont de Nemours and Company, Legal Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US).		(81) Designated States: JP, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: COMPOSITIONS OF DIFLUOROMETHANE, PENTAFLUOROETHANE, 1,1,1,2-TETRAFLUOROETHANE AND HY- DROCARBONS (57) Abstract The present invention relates to azeotrope-like compression refrigerant compositions consisting essentially of difluoromethane (HFC-32), pentafluoroethane (HFC-125), 1,1,1,2-tetrafluoroethane (HFC-134a) and 0.5-5 weight percent of a hydrocarbon selected from the group consisting of: n-butane; isobutane; n-butane and 2-methylbutane; n-butane and n-pentane; isobutane and 2-methylbutane; and isobutane and n-pentane.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

TITLE

COMPOSITIONS OF DIFLUOROMETHANE, PENTAFLUOROETHANE, 1,1,1,2-TETRAFLUOROETHANE AND HYDROCARBONS

5

FIELD OF THE INVENTION

The present invention relates to azeotrope-like compositions consisting essentially of difluoromethane, pentafluoroethane, 1,1,1,2-tetrafluoroethane and a hydrocarbon selected from the group consisting of: n-butane; isobutane; n-butane and 2-methylbutane; n-butane and n-pentane; isobutane and 2-methylbutane; and isobutane and n-pentane.

BACKGROUND

In recent years it has been pointed out that certain kinds of fluorinated hydrocarbon refrigerants released into the atmosphere may adversely affect the stratospheric ozone layer. Although this proposition has not yet been completely established, there is a movement toward the control of the use and the production of certain chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) under an international agreement. Accordingly, there is a demand for the development of refrigerants that have a lower ozone depletion potential than conventional CFC and HCFC-based refrigerants while still achieving an acceptable performance in refrigeration applications. Hydrofluorocarbons (HFCs) are gaining acceptance as replacements for CFCs and HCFCs as HFCs contain no chlorine and therefore have zero ozone depletion potential.

Mineral oils and alkylbenzenes have been conventionally used as lubricants in CFC-based refrigeration systems. However, the lack of solubility of these lubricants in HFC-based refrigerants has precluded their use and necessitated development and use of alternative lubricants for HFC-based refrigeration systems, which utilize polyalkylene glycols (PAGs) and polyol esters (POEs). A lubricant change from mineral oil or alkyl benzene to POE or PAG lubricants (which increases expenses in the refrigeration industry) is required when the HFC mixtures are used to replace CFC-based refrigerants. While the PAGs and POEs are suitable lubricants for HFC-based refrigeration systems, they

are extremely hygroscopic and can absorb several thousand ppm (parts per million) of water on exposure to moist air. This absorbed moisture leads to problems in the refrigeration system, such as formation of acids which cause corrosion of the refrigeration system and formation of intractable sludges. In contrast, mineral oils and alkylbenzenes are much less hygroscopic and have low solubility, less than 100 ppm, for water. Additionally, PAG and POE lubricants are considerably more expensive than the hydrocarbon lubricants, typically on the order of three to six times more expensive. Consequently, there is a need and an opportunity to resolve this solubility problem so that the refrigeration industry may utilize mineral oil and alkylbenzene lubricants with HFC-based refrigerants.

In refrigeration apparatus, refrigerant may be lost during operation through leaks in shaft seals, hose connections, soldered joints and broken lines. In addition, the refrigerant may be released to the atmosphere during maintenance procedures on refrigeration equipment. If the refrigerant is not a pure component or an azeotropic or azeotrope-like composition, the refrigerant composition may change when leaked or discharged to the atmosphere from the refrigeration apparatus, which may cause the refrigerant remaining in the equipment to become flammable or to exhibit unacceptable refrigeration performance. Accordingly, it is desirable to use as a refrigerant a single fluorinated hydrocarbon or an azeotropic or azeotrope-like composition which fractionates to a negligible degree upon leak from a refrigeration apparatus.

In refrigeration applications where the potential of fire or fire's toxic byproducts are a concern, it is desirable for refrigerant compositions to be nonflammable in both liquid and vapor phases, when charging fresh refrigerant to a system or after refrigerant has leaked from a system.

The refrigerants industry has strived to solve some of these problems, and the following disclosures are evidence of such intent:

o Powell et al. in World Intellectual Property Organization international publication WO 9603473A1 disclose a composition for use in a heat transfer device of: (A) at least one hydrofluorocarbons selected from difluoromethane and 1,1,1-trifluoroethane, (B) pentafluoroethane, (C) at least one

hydrocarbon, and optionally (D) at least one hydrofluorocarbon selected from 1,1,1,2-tetrafluoroethane and 1,1,2,2-tetrafluoroethane.

o Pearson in US patent number 5688432 discloses a refrigerant comprising pentafluoroethane, tetrafluoroethane, a hydrocarbon selected from isobutane and propane and optionally octafluoropropane.

o Hisanori et al. in Japan unexamined patent publication Hei 9-25480 disclose a refrigerant composition of difluoromethane, 1,1,1,2-tetrafluoroethane, pentafluoroethane and isobutane.

o Kasuo in European patent application publication EP 0 659 862 A1 discloses a refrigerant composition of difluoromethane, pentafluoroethane, 1,1,1,2-tetrafluoroethane and n-pentane.

o Kazuo in Japan unexamined patent publication Hei 6-220430 disclose a refrigerant composition of difluoromethane, pentafluoroethane, 1,1,1,2-tetrafluoroethane and n-pentane.

o Shiflett in US 5185094 discloses a refrigerant composition of pentafluoroethane, difluoromethane and tetrafluoroethane.

o Kinne et al. in DE 4226431 disclose a 1,1,1,2-tetrafluoroethane refrigerant composition containing 10-20 volume percent of a hydrocarbon.

o Bivens et al. in US 5616276 disclose a refrigerant composition of chlorodifluoroethane, pentafluoroethane, and propane.

o Han et al. in WO 9715637 disclose refrigerant compositions of incombustible halogenated compounds and combustible, essentially hydrocarbon, compounds.

Accordingly, there is a need in the refrigeration industry for compositions that are non-ozone depleting, nonflammable, and essentially non-fractionating azeotrope-like compositions. Additionally, there is a need in the refrigeration industry for compositions that offer improved return of conventional-refrigeration lubricating oils from non-compressor to compressor zones in compression-refrigeration apparatus, as well as superior refrigeration performance.

30

SUMMARY

The compositions of the present invention satisfy the aforementioned needs confronting the refrigeration industry. The present compositions are useful

as refrigerants and in particular as HCFC-22 alternatives. Unlike compositions containing propane and pentane, compositions of the present invention are non-flammable in both liquid and vapor phases, as initially formulated and during leakage. The present invention relates to azeotrope-like compositions consisting essentially of 1-19 weight percent difluoromethane (HFC-32), 25-60 weight percent pentafluoroethane (HFC-125), 24-60 weight percent 1,1,1,2-tetrafluoroethane (HFC-134a) and 0.5-5 weight percent of a hydrocarbon, said hydrocarbon selected from the group consisting of: n-butane; isobutane; n-butane and 2-methylbutane; n-butane and n-pentane; isobutane and 2-methylbutane; and isobutane and n-pentane.

DETAILED DESCRIPTION

The azeotrope-like compositions of the present invention consist essentially of difluoromethane (HFC-32, CH_2F_2 , normal boiling point of -51.7°C), pentafluoroethane (HFC-125, CF_3CHF_2 , normal boiling point of -48.5°C), 1,1,1,2-tetrafluoroethane (HFC-134a, CF_3CHF_2 , normal boiling point of -26.1°C) and a hydrocarbon selected from the group consisting of: n-butane ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$, normal boiling point of -0.5°C); isobutane ($\text{CH}(\text{CH}_3)_3$, normal boiling point of -11.8°C); n-butane and 2-methylbutane ($\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)_2$, normal boiling point of 27.9°C); n-butane and n-pentane ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$, normal boiling point of 35.9°C); isobutane and 2-methylbutane; and isobutane and n-pentane.

The azeotrope-like compositions of the present invention consist essentially of 1-19 weight percent difluoromethane, 25-60 weight percent pentafluoroethane, 24-60 weight percent 1,1,1,2-tetrafluoroethane and 0.5-5 weight percent of a hydrocarbon, said hydrocarbon selected from the group consisting of: n-butane; isobutane; n-butane and 2-methylbutane; n-butane and n-pentane; isobutane and 2-methylbutane; and isobutane and n-pentane. The preferred azeotrope-like compositions of the present invention consist essentially of 1-15 weight percent difluoromethane, 30-50 weight percent pentafluoroethane, 30-50 weight percent 1,1,1,2-tetrafluoroethane and 1-4 weight percent of the aforementioned hydrocarbons. The most preferred azeotrope-like compositions of the present invention consist essentially of 1-9 weight percent difluoromethane

(HFC-32), 30-50 weight percent pentafluoroethane (HFC-125), 30-50 weight percent 1,1,1,2-tetrafluoroethane (HFC-134a) and 1-4 weight percent of the aforementioned hydrocarbons.

By azeotrope-like composition is meant a constant boiling, or substantially
5 constant boiling, liquid admixture of two or more substances that behaves as a single substance. One way to characterize an azeotrope-like composition is that the vapor produced by partial evaporation or distillation of the liquid has substantially the same composition as the liquid from which it was evaporated or distilled. Essentially, the admixture distills/refluxes without substantial
10 composition change. Another way to characterize an azeotrope-like composition is that the bubble point vapor pressure and the dew point vapor pressure of the composition at a particular temperature are substantially the same. Herein, a composition is azeotrope-like if, after 50 weight percent of the composition is removed such as by evaporation or boiling off, the difference in vapor pressure
15 between the original composition and the composition remaining after 50 weight percent of the original composition has been removed is less than 10 percent.

By effective amount is meant the amount of each component of the inventive compositions which, when combined, results in the formation of an azeotrope-like composition. This definition includes the amounts of each
20 component, which amounts may vary depending on the pressure applied to the composition so long as the azeotrope-like compositions continue to exist at the different pressures, but with possible different boiling points. Therefore, effective amount includes the amounts, such as may be expressed in weight percentages, of each component of the compositions of the instant invention which form an
25 azeotrope-like compositions at temperatures or pressures other than as described herein.

The azeotrope-like compositions of the present invention can be prepared by any convenient method including mixing or combining effective amounts of components. A preferred method is to weigh the desired component amounts and
30 thereafter combine them in an appropriate container.

A surprising result, and an important feature of the present compositions, is that they remain nonflammable in both the vapor and liquid phases before and

after the compositions leak from a container. Based on standard flammability test method ASTM 681 at 100°C, the following flammability limits have been determined:

5	Composition	Flammability Limit (Wt%)
	HFC-125/HFC-32	57 % HFC-32
	HFC-134a/HFC-32	33 % HFC-32
	HFC-125/n-butane	6 % n-butane
	HFC-134a/n-butane	3 % n-butane

10

The data show compositions with a higher amount of HFC-125 can tolerate more hydrocarbon and still be nonflammable. Also, HFC-32 is about 10 times less flammable than hydrocarbons. To give an indication of mixture flammability, the following formula gives an approximation of the “total equivalent hydrocarbon” (TEH) present in mixtures that contain both HFC-32 and hydrocarbons: $TEH = HC + R32/10$, where TEH = Total Equivalent Hydrocarbon in weight percent, HC = weight percent hydrocarbon in a mixture, and R32 = weight percent HFC-32 in a mixture. For the compositions of the present invention, it is useful to relate the amount of HFC-125 in the mixture to flammability because HFC-125 has some degree of flame suppression. Table 1 indicates the flammability limit of a mixture containing both HFC-32 and hydrocarbons based on HFC-125 composition and TEH.

20

TABLE 1

Weight Percent HFC-125 in HFC-32/HFC-125/HFC- 134a/HC Mixture	Maximum Weight Percent TEH To Be Nonflammable
10	3.0
20	3.3
30	3.7
40	4.0
50	4.3

60	4.7
70	5.0
80	5.5
90	6.0

Additives known in the refrigerants field such as lubricants, corrosion inhibitors, surfactants, stabilizers, anti-foam agents, dyes and other appropriate materials may be added to, and used in the presence of, the present compositions of the invention for a variety of purposes, provide that such additives do not have an adverse influence on the present compositions for their intended application or change the basic and novel characteristics of the present invention as claimed.

Although the present specification is directed to use of the present azeotrope-like compositions as compression refrigerants, the present compositions may also find utility as cleaning agents, expansion agents for polyolefins and polyurethanes (polymer foam blowing agents), aerosol propellants, heat transfer media, gaseous dielectrics, power cycle working fluids, polymerization media, particulate removal fluids, carrier fluids, buffing abrasive agents and displacement drying agents.

15

EXAMPLES

Specific examples illustrating the present invention are given below.

Unless otherwise stated therein, all percentages are by weight.

20 **EXAMPLE 1: Impact of Vapor Leakage on Compositional Change at 25°C of a HFC-32, HFC-125, HFC-134a, n-butane and optionally 2-methylbutane or n-pentane Composition**

A vessel is charged to 90 volume % full with an initial composition of HFC-32, HFC-125, HFC-134a, n-butane and optionally 2-methylbutane or n-pentane at 25°C. The initial liquid and vapor compositions are measured by gas chromatography. The composition is allowed to leak from the vessel, while the temperature is held constant at 25°C, until 50 weight percent of the initial composition is removed, at which time the liquid and vapor compositions

remaining in the vessel are again measured. The vessel is then allowed to continue to leak until all the liquid is gone. In all cases, liquid was gone after about 97wt% was removed. The results are summarized in Table 2 below. All compositions are given in weight %.

5

TABLE 2

	Initial Liquid	Initial Vapor	50% Leak - Liquid	50% Leak - Vapor	97% Leak - Liquid	97% Leak - Vapor
HFC-32	9.0	12.8	6.5	9.9	1.0	1.9
HFC-125	46.0	55.6	38.8	49.9	10.7	18.1
HFC-134a	42.5	29.1	52.3	37.6	87.3	78.4
n-butane	2.5	2.5	2.4	2.6	1.0	1.6
TEH	3.4	3.8	3.0	3.6	1.1	1.8
HFC-32	10.0	14.2	7.3	10.9	1.1	2.1
HFC-125	45.0	54.3	37.9	48.8	10.4	17.6
HFC-134a	42.5	29.0	52.4	37.6	87.5	78.7
n-butane	2.5	2.5	2.4	2.7	1.0	1.6
TEH	3.5	3.9	3.1	3.8	1.1	1.8
HFC-32	10.0	13.9	7.3	11.0	1.0	1.9
HFC-125	45.0	52.3	38.8	49.2	10.3	17.7
HFC-134a	42.5	28.3	52.9	37.3	88.7	80.3
propane	2.5	5.5	1.0	2.5	0.0	0.1
TEH	3.5	6.9*	1.7	3.6	0.1	0.3
HFC-32	10.0	14.4	7.1	11.0	0.7	1.4
HFC-125	45.0	55.1	37.3	49.1	7.6	14.1
HFC-134a	42.5	29.3	51.9	38.2	72.7	78.5
n-pentane	2.5	1.2	3.6	1.7	19.0	6.0

TEH	3.5	2.6	4.3*	2.8	19.1*	6.1*
HFC-32	10	14.2	7.3	10.9	1.0	2.0
HFC-125	45	54.5	37.8	48.9	10.1	17.1
HFC-134a	42.5	29.0	52.3	37.7	86.1	78.2
n-butane	2.0	2.0	1.9	2.1	0.9	1.4
2-mbutane	0.5	0.3	0.7	0.4	1.9	1.3
TEH	3.5	3.7	3.3	3.6	2.9	2.9
HFC-32	5.0	8.0	3.2	5.4	0.2	0.5
HFC-125	32.2	43.9	24.1	35.5	3.7	6.8
HFC-134a	60.0	45.4	69.9	56.3	93.1	90.0
n-butane	2.0	2.3	1.7	2.2	0.5	0.8
2-mbutane	0.8	0.4	1.1	0.6	2.5	1.9
TEH	2.9	3.5	3.1	3.3	3.0	2.8
HFC-32	5	7.2	3.6	5.5	0.5	1.0
HFC-125	50	61.0	41.8	54.3	11.2	18.8
HFC-134a	42.7	29.7	52.2	38.0	85.1	77.5
n-butane	1.8	1.9	1.7	1.9	0.9	1.2
n-pentane	0.5	0.2	0.7	0.3	2.3	1.5
TEH	2.8	2.9	2.8	2.9	3.2	2.8

* Compositions are flammable based on TEH analysis

When TEH values of this Example are compared to Table 1, results show compositions of the precent invention are essentially nonflammable, initially and as contents are completely leaked out of the container. Data also show addition of a higher boiling hydrocarbon such as 2-methylbutane reduces initial vapor phase flammability when compared to using only n-butane. Compositions containing propane are flammable initially in the vapor phase and compositions containing n-pentane become flammable in the liquid and/or vapor phases as liquid is removed.

EXAMPLE 2: Impact of Vapor Leakage on Compositional Change at 25°C of a HFC-32, HFC-125, HFC-134a, isobutane and optionally 2-methylbutane or n-pentane Composition

- 5 A vessel is charged to 90 volume % full with an initial composition of HFC-32, HFC-125, HFC-134a, isobutane and optionally 2-methylbutane or n-pentane at 25°C. The initial liquid and vapor compositions are measured by gas chromatography. The composition is allowed to leak from the vessel, while the temperature is held constant at 25°C, until 50 weight percent of the initial
- 10 composition is removed, at which time the liquid and vapor compositions remaining in the vessel are again measured. The vessel is then allowed to continue to leak until all the liquid is gone. In all cases, liquid was gone after about 97 wt% was removed. The results are summarized in Table 3 below. All compositions are given in weight %.

15

TABLE 3

	Initial Liquid	Initial Vapor	50% Leak - Liquid	50% Leak - Vapor	97% Leak - Liquid	97% Leak - Vapor
HFC-32	10.0	12.7	6.5	9.8	1.0	1.9
HFC-125	45.0	55.3	39.0	49.9	10.7	18.1
HFC-134a	42.5	29.0	52.4	37.5	88.0	79.3
isobutane	2.5	3.0	2.1	2.8	0.3	0.7
TEH	3.5	4.3	2.7	3.8	0.4	0.9
HFC-32	10.0	14.0	7.4	10.9	1.1	2.2
HFC-125	47.0	55.7	40.2	50.8	11.8	19.8
HFC-134a	40.5	27.3	50.3	35.5	86.7	77.2
isobutane	2.5	3.0	2.1	2.8	0.4	0.8
TEH	3.5	4.4	2.8	3.9	0.5	1.0

HFC-32	10.0	14.2	7.2	10.9	1.0	2.0
HFC-125	45.5	54.2	38.0	48.9	10.0	17.0
HFC-134a	42.5	29.0	52.4	37.6	86.4	78.9
isobutane	2.0	2.4	1.7	2.2	0.4	0.6
n-pentane	0.5	0.2	0.7	0.4	2.2	1.5
TEH	3.5	4.0	3.1	3.7	2.7	2.3
HFC-32	15.0	23.0	9.9	16.5	0.8	1.6
HFC-125	24.0	32.3	18.1	26.6	2.7	5.0
HFC-134a	60.0	43.6	71.1	55.9	95.4	92.4
isobutane	0.5	0.8	0.3	0.6	0.0	0.0
2-mbutane	0.5	0.3	0.6	0.4	1.1	1.0
TEH	2.5	3.4	1.9	2.6	1.2	1.2
HFC-32	19	24.6	15.1	20.7	3.7	6.5
HFC-125	50	55.8	45.3	53.2	19.0	29.2
HFC-134a	30	18.8	38.5	25.3	74.9	62.7
isobutane	0.5	0.6	0.4	0.5	0.1	0.2
n-pentane	0.5	0.2	0.7	0.3	2.3	1.4
THE	2.9	3.3	2.6	2.9	2.8	2.2

When TEH values of this Example are compared to Table 1, results show compositions are essentially nonflammable, initially and as contents are completely leaked out of the container. Data also show addition of a higher boiling hydrocarbon such as n-pentane reduces initial vapor phase flammability when compared to using only isobutane.

EXAMPLE 3: Impact of Vapor Leakage on Vapor Pressure at 25°C

A vessel is charged with an initial composition at 25°C, and the initial vapor pressure of the composition is measured. The composition is allowed to leak from the vessel while the temperature is held constant at 25°C until 50 weight

percent of the initial composition is removed, at which time the vapor pressure of the composition remaining in the vessel is measured. The results are summarized in Table 4 below.

5

TABLE 4

Composition (Wt%)	Initial Pressure (kPa)	Pressure After Leak (kPa)	%Change in Pressure
HFC-32/HFC-125/HFC-134/n-butane			
1.0/60.0/34.0/5.0	1101	1042	5.4
19.0/56.5/24.0/0.5	1348	1272	5.6
9.0/46.0/42.5/2.5	1134	1044	7.9
5.0/34.0/60.0/1.0	979	891	9.0
16.0/57.0/24.0/3.0	1318	1245	5.5
19.0/25.0/51.0/5.0	1149	1038	9.7
10.0/45.0/42.5/2.5	1142	1051	8.0
HFC-32/HFC-125/HFC-134a/isobutane			
1.0/60.0/34.0/5.0	1123	1065	5.2
19.0/56.5/24.0/0.5	1351	1275	5.6
9.0/46.0/42.5/2.5	1147	1055	8.0
5.0/34.0/60.0/1.0	985	895	9.1
16.0/57.0/24.0/3.0	1333	1261	9.5
19.0/25.0/51.0/5.0	1172	1059	9.6
10.0/45.0/42.5/2.5	1155	1062	8.1
10.0/47.0/40.5/2.5	1167	1078	7.6
HFC-32/HFC-125/HFC-134a/n-butane/2-methylbutane			
1.0/60.0/34.0/0.5/4.5	1064	985	7.4
19.0/56.5/24.0/0.5/0.5	1342	1264	5.8
9.0/46.0/42.5/1.0/1.5	1120	1024	8.6
5.0/34.0/60.0/0.5/0.5	974	885	9.1
16.0/57.0/24.0/2.0/1.0	1310	1231	6.0
19.0/25.0/51.0/4.5/0.5	1145	1031	10.0
10.0/45.0/42.5/2.0/0.5	1138	1044	8.3
HFC-32/HFC-125/HFC-134a/n-			

butane/n-pentane			
1.0/60.0/34.0/0.5/4.5	1058	975	7.8
19.0/56.5/24.0/0.5/0.5	1341	1262	5.9
9.0/46.0/42.5/1.0/1.5	1118	1020	8.8
5.0/34.0/60.0/0.5/0.5	973	885	9.0
16.0/57.0/24.0/2.0/1.0	1309	1229	6.1
19.0/25.0/51.0/4.5/0.5	1145	1030	10.0
10.0/45.0/42.5/2.0/0.5	1137	1043	8.3
HFC-32/HFC-125/HFC-134a/isobutane/2-methylbutane			
1.0/60.0/34.0/0.5/4.5	1066	987	7.4
19.0/56.5/24.0/0.5/0.5	1345	1267	5.8
9.0/46.0/42.5/1.0/1.5	1125	1028	8.6
5.0/34.0/60.0/0.5/0.5	976	887	9.1
16.0/57.0/24.0/2.0/1.0	1320	1242	5.9
19.0/25.0/51.0/4.5/0.5	1167	1050	10.0
10.0/45.0/42.5/2.0/0.5	1147	1053	8.2
HFC-32/HFC-125/HFC-134a/isobutane/n-pentane			
1.0/60.0/34.0/0.5/4.5	1060	977	7.8
19.0/56.5/24.0/0.5/0.5	1344	1265	5.9
9.0/46.0/42.5/1.0/1.5	1122	1024	8.7
5.0/34.0/60.0/0.5/0.5	975	886	9.1
16.0/57.0/24.0/2.0/1.0	1319	1238	6.1
19.0/25.0/51.0/4.5/0.5	1166	1049	10.0
10.0/45.0/42.5/2.0/0.5	1147	1051	8.4
HFC-32/HFC-125/HFC-134a/propane (10.0/45.0/42.5/2.5)	1247	1096	12.1

The results of this Example show azeotrope-like compositions of the present invention are present as after 50 wt% of an original composition is removed, the vapor pressure of the remaining composition is changed by less than about 10% of the vapor pressure of the original composition, at a temperature of 25°C. Reducing the amount of HFC-32 in the compositions may result in a more azeotrope-like mixture. Compositions containing propane are not azeotrope-like.

EXAMPLE 4: Effect of Hydrocarbon Addition on Fractionation

A vessel is charged 90% full by volume with an initial composition at 25°C, and the initial vapor pressure of the composition is measured. The composition is allowed to leak from the vessel, while the temperature is held constant at 25°C until 50 weight percent of the initial composition is removed, at which time the vapor pressure of the composition remaining in the vessel is measured. The results are summarized in Table 5 below.

TABLE 5

Composition (Wt%)	Initial Pressure (kPa)	Pressure After Leak (kPa)	% Change in Pressure
HFC-32/HFC-125/HFC-134a (refrigerant "R407C") (23/25/52)	1179	1055	10.5
HFC-32/HFC-125/HFC-134a (20/40/40)	1241	1135	8.5
HFC-32/HFC-125/HFC-134a/n-butane (15/42/41.5/1.5)	1193	1093	8.4
HFC-32/HFC-125/HFC-134a/n-butane (10/45/42.5/2.5)	1142	1051	8.0
HFC-32/HFC-125/HFC-134a/n-butane (5/48/44/3)	1083	1005	7.2
HFC-32/HFC-125/HFC-134a/isobutane (15/42/41.5/1.5)	1200	1099	8.4
HFC-32/HFC-125/HFC-134a/isobutane (10/45/42.5/2.5)	1155	1062	8.1
HFC-32/HFC-125/HFC-134a/isobutane (5/48/44/3)	1098	1017	7.4

10

The results of this Example show that fractionation is reduced; compositions become more azeotrope-like as HFC-32 is replaced with the present hydrocarbons. Compositions of the present invention also have less fractionation than refrigerant composition R407C.

15

EXAMPLE 5 :Refrigerant Performance

The following table shows the performance of compositions of the present invention. The data are based on the following conditions.

5	Evaporator temperature	8.9°C
	Condenser temperature	46.1°C
	Subcool temperature	39.4°C
	Return gas temperature	18.3°C
	Compressor clearance volume is 4%	
10	Compressor isentropic efficiency is 75%	

Capacity is intended to mean the change in enthalpy of the refrigerant in the evaporator per pound of refrigerant circulated, i.e. the heat removed by the refrigerant in the evaporator per time. Coefficient of Performance (COP) is
 15 intended to mean the ratio of the capacity to compressor work, It is a measure of refrigerant energy efficiency. Results are shown in Table 6 below.

TABLE 6

Composition (wt%)	Evap Press (kPa)	Cond Press (kPa)	Comp Disch. T (°C)	COP	Capacity (Watts)
HFC-125/HFC-134a/n-butane (46.5/50.0/3.5)	572	1627	65.6	5.79	5317
HFC-125/HFC-134a/isobutane (32.0/64.0/4.0)	529	1516	64.3	5.87	5014
HFC-32/HFC-125/HFC-134a/n- butane (10.0/45.0/42.5/2.5)	658	1852	69.3	5.74	6058
HFC-32/HFC-125/HFC-134a/n- butane/2-methylbutane (5.0/32.0/60.0/2.0/1.0)	550	1582	67.3	5.89	5287
HFC-32/HFC-125/HFC-134a/n- butane/n-pentane (1.0/60.0/34.0/4.0/1.0)	634	1770	65.1	5.64	5595

HFC-32/HFC-125/HFC-134a/isobutane (10.0/47.0/40.5/2.5)	674	1892	67.9	5.70	6111
HFC-32/HFC-125/HFC-134a/isobutane/2-methylbutane (15.0/24.0/60.0/0.5/0.5)	596	1722	71.4	5.90	5829
HFC-32/HFC-125/HFC-134a/isobutane/n-pentane (19.0/50.0/30.0/0.5/0.5)	754	2101	71.5	5.67	6820

Results of this Example show that compositions of the present invention exhibit either higher capacity, efficiency or both when compared to compositions which do not contain HFC-32.

5

EXAMPLE 6: Oil Return Test with Present Compositions

Oil return was tested in an oil-return apparatus as follows. Liquid refrigerant was fed from a pressurized cylinder through copper tubing to a heater where it was vaporized. The refrigerant vapor then passed through a pressure regulator and metering valve to control flow at a constant rate of 1,000-1,100 cc per minute and 1 atm pressure. The refrigerant vapor was fed to another copper tube 180 cm in length and 0.635 cm outer diameter formed into a U-shape placed in a constant temperature bath. The U-shaped tube (U-tube) began with a straight vertical section 37 cm long then bent to a horizontal section 27 cm long at the bottom of the bath. The tube then rose vertically in a zig-zag pattern with four 23 cm lengths, followed by another vertical straight section 23 cm long. The U-tube was filled with 10 grams of oil, optionally containing oil-return agent and oil-return-agent carrier, which was added to the U-tube through the 37 cm vertical tube. Vapor refrigerant passed slowly through the oil in the U-tube. Refrigerant and oil exiting the U-tube was collected in a receiver and refrigerant allowed to evaporate. Oil was then weighed to determine how much was carried out of the U-tube by the refrigerant.

R407C refrigerant (23 weight % HFC-32, 25 weight % HFC-125 and 52 weight % HFC-134a) was placed in the refrigerant cylinder. Suniso® 3GS mineral oil was placed in the copper U-tube, wherein total oil and oil-return agent,

and oil-return-agent carrier equaled 10 grams. The constant temperature bath was held at a temperature of 0°C. Refrigerant vapor was fed through the U-tube at a flow rate of 1,100 cubic centimeters per minute and weight of oil in the receiver measured at 6, 10, and 20 minute time intervals. Refrigerant compositions of the present invention were then tested with Suniso® 3GS. Data are shown in Table 7 below.

TABLE 7: Oil Return with 3GS Mineral Oil

<u>Refrigerant</u>	<u>Composition (Wt%)</u>	<u>Weight % of Oil Returned</u>		
		<u>6 Min</u>	<u>10 Min</u>	<u>20 Min</u>
R407C (HFC-32/HFC-125/HFC-134a)	23/25/52	11.1	22.3	32.3
HFC-32/HFC-125/HFC-134a/n-butane	10/45/42.5/2.5	12.9	25.2	32.9
HFC-32/HFC-125/HFC-134a/isobutane	10/47/40.5/2.5	12.5	23.0	34.2
HFC-32/HFC-125/HFC-134a/n-butane/2-methyl butane	5/32/60/2/1	16.1	26.9	35.5
HFC-32/HFC-125/HFC-134a/n-butane/n-pentane	1/60/34/4/1	22.5	31.5	39.7
HFC-32/HFC-125/HFC-134a/isobutane/2-methylbutane	14.5/24/60/1.0/0.5	12.1	23.0	32.4
HFC-32/HFC-125/HFC-134a/isobutane/n-pentane	19/50/30/0.5/0.5	13.8	24.2	33.5
HFC-32/HFC-125/HFC-134a/n-butane with enhanced 3GS*	10/45/42.5/2.5	28.2	33.3	38.4
HFC-32/HFC-125/HFC-134a with enhanced 3GS*	10/45/45	28.5	33.0	38.1

* 3GS oil is enhance with 0.4 wt% Zonyl®PHS plus 3% Isopar®H plus 200 ppm Dow 200 antifoam agent. Zonyl®PHS is sold by E. I. du Pont de Nemours & Co. and is a random copolymer made from 40 weight percent $\text{CH}_2=\text{C}(\text{CH}_3)\text{CO}_2\text{CH}_2\text{CH}_2(\text{CF}_2\text{CF}_2)_{m'}\text{F}$, wherein m' is from 1 to 12, primarily 2 to 8, and 60 weight percent lauryl methacrylate ($\text{CH}_2=\text{C}(\text{CH}_3)\text{CO}_2(\text{CH}_2)_{11}\text{CH}_3$).
5 Isopar®H is a high purity iso-parafinic hydrocarbon with low aromatics sold by Exxon Chemical

Results from Example 6 show in all cases, oil return of the compositions
10 of the present invention is improved versus R407C. Oil return increases with increased hydrocarbon concentration. Addition of polymeric oil return agent Zonyl®PHS to 3GS oil further improves oil return.

WHAT IS CLAIMED IS:

1. An azeotrope-like composition consisting essentially of 1-19 weight percent difluoromethane (HFC-32), 25-60 weight percent pentafluoroethane (HFC-125), 24-60 weight percent 1,1,1,2-tetrafluoroethane (HFC-134a) and 0.5-5 weight percent of a hydrocarbon selected from the group consisting of: n-butane; isobutane; n-butane and 2-methylbutane; n-butane and n-pentane; isobutane and 2-methylbutane; and isobutane and n-pentane.
2. The azeotrope-like composition of claim 1 consisting essentially of 1-15 weight percent difluoromethane (HFC-32), 30-50 weight percent pentafluoroethane (HFC-125), 30-50 weight percent 1,1,1,2-tetrafluoroethane (HFC-134a) and 1-4 weight percent of said hydrocarbon.
3. The azeotrope-like composition of claim 1 consisting essentially of 1-9 weight percent difluoromethane (HFC-32), 30-50 weight percent pentafluoroethane (HFC-125), 30-50 weight percent 1,1,1,2-tetrafluoroethane (HFC-134a) and 1-4 weight percent of said hydrocarbon.
4. The azeotrope-like composition of claim 1, wherein the hydrocarbon is 0.5-5 weight percent of:
 - a) n-butane, said azeotrope-like composition having a vapor pressure of 979 kPa-1348 kPa at a temperature of 25°C; or
 - b) isobutane, said azeotrope-like composition having a vapor pressure of 985 kPa-1351 kPa at a temperature of 25°C; or
 - c) n-butane and 2-methylbutane, said azeotrope-like composition having a vapor pressure of 974 kPa-1342 kPa at a temperature of 25°C; or
 - d) n-butane and n-pentane, said azeotrope-like composition having a vapor pressure of 973 kPa-1341 kPa at a temperature of 25°C; or
 - e) isobutane and 2-methylbutane, said azeotrope-like composition having a vapor pressure of 976 kPa-1345 kPa at a temperature of 25°C; or

- f) isobutane and n-pentane, said azeotrope-like composition having a vapor pressure of 975 kPa-1344 kPa at a temperature of 25°C, and wherein after 50 weight percent of said azeotrope-like composition has evaporated, the vapor pressure of the remaining composition has changed by 10 percent or less.

5. A process for producing refrigeration, comprising condensing a composition of Claims 1, 2, 3, or 4, and thereafter evaporating said composition in the vicinity of the body to be cooled.
6. A process for producing heat, comprising condensing a composition of Claims 1, 2, 3, or 4, in the vicinity of the body to be heated, and thereafter evaporating said composition.
7. A process for reducing the change in vapor pressure during evaporation of a refrigerant composition, consisting essentially of difluoromethane (HFC-32), pentafluoroethane (HFC-125) and 1,1,1,2-tetrafluoroethane (HFC-134a), comprising removing said composition in the presence of 0.5-5 weight percent, based on the total composition weight, of a hydrocarbon selected from the group consisting of: n-butane; isobutane; n-butane and 2-methylbutane; n-butane and n-pentane; isobutane and 2-methylbutane; and isobutane and n-pentane.

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C09K5/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C09K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 96 03473 A (MURPHY FREDERICK THOMAS ; CORR STUART (GB); ICI PLC (GB); MORRISON) 8 February 1996 (1996-02-08) cited in the application page 4, line 4 - line 8; claims 12-16; examples 1-3; table 2 page 1, line 2 - page 5, line 23	1, 2, 4-7
Y	---	3
X	WO 97 15637 A (HAN LIZHONG ; UNIV TSINGHUA (CN); ZHAO XIAOYU (CN); YE MAO (CN); ZH) 1 May 1997 (1997-05-01) cited in the application abstract	1-14
Y	---	1-14
	--- -/--	



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- "&" document member of the same patent family

Date of the actual completion of the international search

21 July 2000

Date of mailing of the international search report

02/08/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

olde Scheper, B

INTERNATIONAL SEARCH REPORT

Inter. Patent Application No

PCT/US 00/07546

--

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	<p>EP 0 659 862 A (SANYO ELECTRIC CO) 28 June 1995 (1995-06-28) cited in the application abstract column 1, line 5 -column 4, line 50; claims 1-8</p> <p>-----</p>	1-14

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 00/07546

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9603473 A	08-02-1996	AU 698733 B	05-11-1998
		AU 2988795 A	22-02-1996
		BR 9508347 A	30-09-1997
		CA 2195411 A	08-02-1996
		EP 0772659 A	14-05-1997
		JP 10503230 T	24-03-1998
WO 9715637 A	01-05-1997	CN 1148613 A	30-04-1997
		CN 1162616 A	22-10-1997
		AU 7276996 A	15-05-1997
EP 0659862 A	28-06-1995	JP 7173460 A	11-07-1995
		CN 1108290 A	13-09-1995
		DE 69410966 D	16-07-1998
		DE 69410966 T	08-10-1998